

# Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

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REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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than in the Upper Floridan; the effects of mixing on  $\text{Ca}^{2+}$  concentrations are not noticeable, and calcite is maintained at equilibrium. Simulation of the predevelopment flow system in this area indicates that small quantities of water flow from the Lower to the Upper Floridan aquifer (Krause, 1982); somewhat larger quantities may now be flowing because of development and pumpage from the Upper Floridan.

Ion exchange may be an alternative explanation for some of the patterns of hydrochemical facies discussed above. In east-central Georgia, the Upper Floridan aquifer is composed primarily of limestone, but even small quantities of clay minerals might be sufficient to exchange the required amounts of  $\text{Na}^+$  for  $\text{Ca}^{2+}$ . As with other geochemical questions unanswered in this report, detailed mineralogical studies are needed to test this hypothesis. Only in the western Florida Panhandle does ion exchange seem the most probable mechanism for developing the hydrochemical facies mapped in the Upper Floridan aquifer. In that area, the normal downgradient change from calcium-magnesium-bicarbonate to mixed facies does not occur. Rather, a mixed-bicarbonate facies evolves, which farther downgradient becomes a sodium-bicarbonate facies. There is a net loss of  $\text{Ca}^{2+}$  in the downgradient direction, which could result from calcite precipitation, as  $\text{HCO}_3^-$  concentrations are very high and calcite is at saturation. The source of additional  $\text{Na}^+$  is probably ion exchange because available chemical data indicate that mineral weathering is not a major source. Infiltration of  $\text{Na}^+$ -rich water is not possible since this is a discharge area for the Upper Floridan. Nor is upward leakage a plausible source, because, except in western Okaloosa County, Fla., the almost impermeable Bucatunna Formation separates the Upper and Lower Floridan aquifers. In addition, throughout most of Santa Rosa County, Fla., the Lower Floridan contains high  $\text{Cl}^-$  and dissolved-solids concentrations (figs. 24, 27), while concentrations of these constituents are low in the Upper Floridan, except in the vicinity of Pensacola Bay. Taken together, the chemical and hydrologic data indicate that ion exchange is the mechanism producing the sodium-bicarbonate facies that occur in the Upper Floridan aquifer in the western panhandle area.

#### MINOR CONSTITUENTS

##### FLUORIDE

The fluoride ( $\text{F}^-$ ) concentration in water in the Upper Floridan aquifer varies from nearly zero near outcrop areas to more than 4 mg/L in western Florida (fig. 28). Over most of the region, the  $\text{F}^-$  concentration is less than 1.0 mg/L, well within the mandatory standard (based on the annual average of maximum daily air

temperatures) of 1.4 to 1.8 mg/L for drinking water in the region (U.S. Environmental Protection Agency, 1975). In coastal areas, mixing of fresh ground water with seawater brings  $\text{F}^-$  concentrations to approximately 1.5 mg/L, depending on the depth of the well and the amount of seawater in the Upper Floridan aquifer.

Water recharging the aquifer system is the principal source of  $\text{F}^-$  in the freshwater parts of the system. In unconfined areas,  $\text{F}^-$  concentrations are very low, reflecting the low concentrations of  $\text{F}^-$  in rainfall: Irwin and Kirkland (1980) reported that  $\text{F}^-$  concentrations in rainfall at Maitland and Ocala, Fla., averaged 0.1 mg/L (range, 0.0 to 0.2 mg/L at Maitland and 0.0 to 0.3 mg/L at Ocala). Where the aquifer system is confined, recharge water contains  $\text{F}^-$  dissolved from carbonate fluorapatites, which are relatively abundant in the Miocene sediments of the system's upper confining unit. Once the  $\text{F}^-$  in recharge water enters the Upper Floridan aquifer, it appears to be chemically conservative. Fluorite ( $\text{CaF}_2$ ) is consistently undersaturated in water samples from the Upper Floridan and should not be controlling  $\text{F}^-$  concentrations. Fluoride-bearing apatites may control  $\text{F}^-$  concentrations, but these minerals form very slowly and are generally highly oversaturated in water samples from wells in the Upper Floridan aquifer (table 9, fig. 29). Anion exchange of  $\text{F}^-$  for hydroxyl ions ( $\text{OH}^-$ ) in apatite is well known (for example, Krauskopf, 1979, p. 74) and probably occurs to some degree in the Upper Floridan. The extent to which anion exchange removes  $\text{F}^-$  from ground water in the Upper Floridan aquifer cannot be determined at this time, owing to lack of data on the quantity and chemical composition of apatite in the aquifer.

It is difficult to prove with available data that equilibrium between ground water and a carbonate fluorapatite phase is (or is not) controlling  $\text{F}^-$  concentrations. The use of WATEQF to calculate the S.I. of various apatite species in water samples from the Upper Floridan aquifer is complicated by several factors: (1) phosphate concentrations were determined in Upper Floridan water samples that had passed through a relatively coarse filter (0.45 micrometer ( $\mu\text{m}$ )), thus allowing whole microorganisms or parts of microorganisms to be analyzed along with "dissolved" phosphate (see later section on "Nutrients"); (2) apatites in nature occur as a solid-solution series containing variable amounts of calcium, sodium, magnesium, strontium, phosphate, carbonate, sulfate, and hydroxide (McClellan and Lehr, 1969; Baturin and others, 1970; McArthur, 1978; Manheim and others, 1980; Gulbrandsen and others, 1984), and each species has a different solubility in ground water (Brown, 1960; Roberson, 1966; Wier and others, 1971; Chien and Black, 1976; Nathan and Sass, 1981); and (3) the composition of apatites in the Floridan aquifer system is not

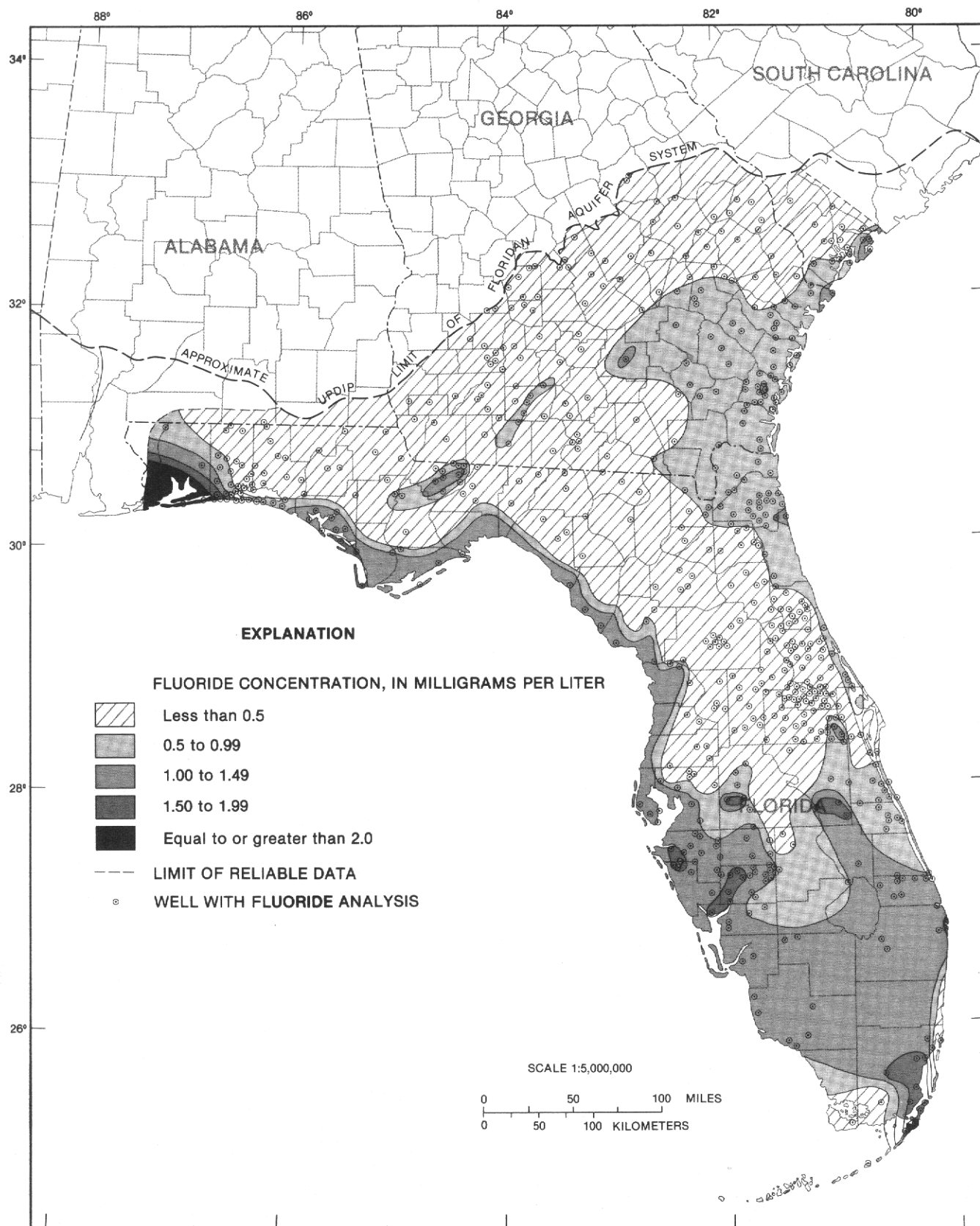


FIGURE 28.—Fluoride concentrations in water from the Upper Floridan aquifer.

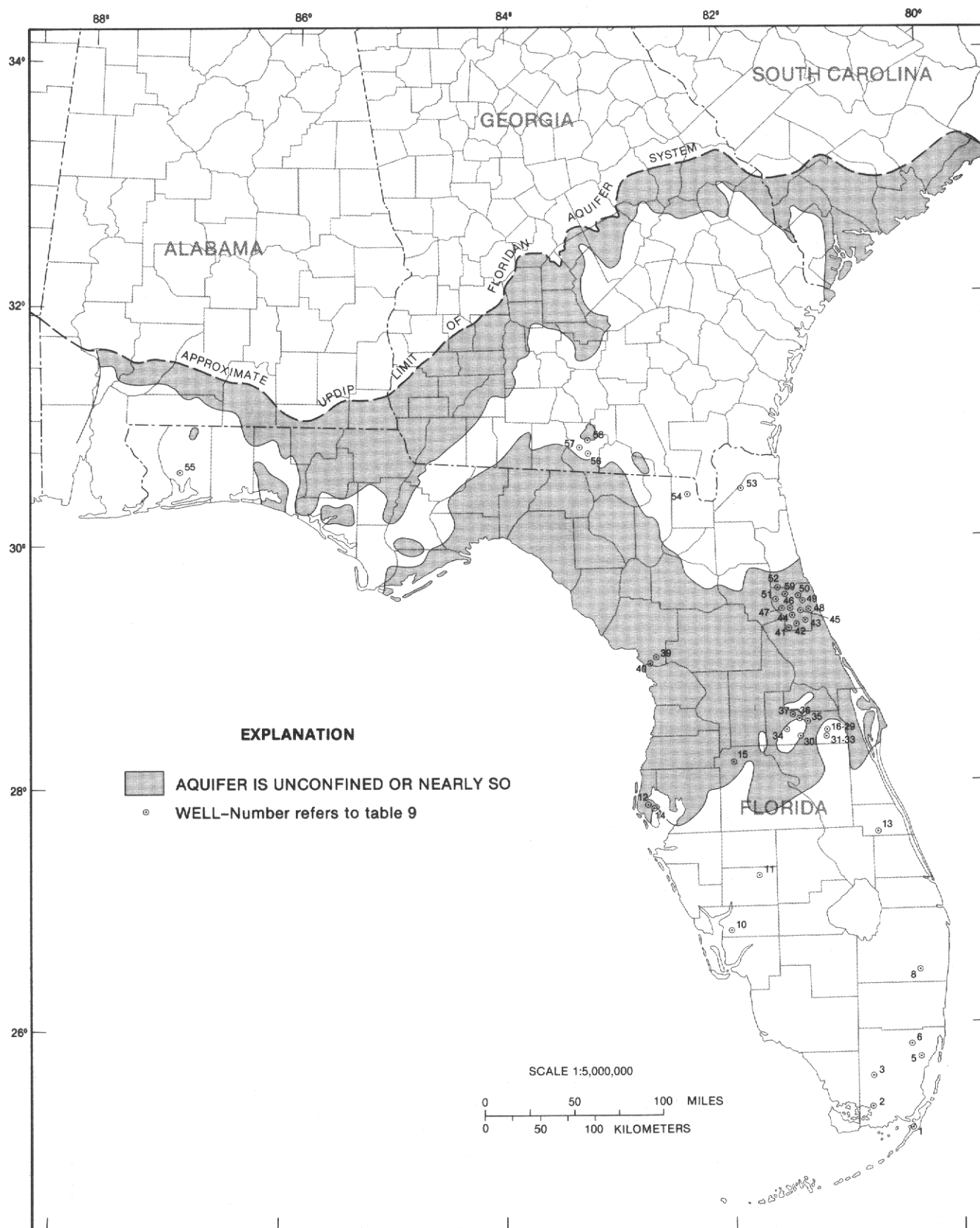


FIGURE 29.—Wells in the Upper Floridan aquifer with water analyses of phosphate and fluoride.

TABLE 9.—Ion activities and saturation indices of apatites calculated by WATEQF using selected chemical analyses of water from wells in the Upper Floridan aquifer

Well number <sup>1</sup>	Water temperature, in °C	-Log <sub>10</sub> ion activity							Saturation index				
		H <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	CO <sub>3</sub> <sup>2-</sup>	F <sup>-</sup>	Fluor-apatite <sup>2</sup>	Hydroxy-apatite <sup>2</sup>	Carbonate fluorapatites <sup>3</sup>		
											Florida	North Carolina	Tennessee
1	27.5	7.90	2.99	2.56	1.27	11.13	4.99	4.25	9.3	0.1	6.6	15.2	13.0
	27.5	7.40	2.99	2.60	1.27	12.22	5.46	4.17	6.1	-3.6	10.8	9.6	7.0
2	29.0	7.70	2.87	2.56	1.22	11.64	5.25	4.44	8.2	-0.9	14.5	13.1	10.7
	25.4	8.15	3.10	2.57	1.29	11.48	5.44	4.86	7.0	-1.4	12.0	10.4	8.1
3	25.0	7.50	3.13	2.77	1.54	12.01	5.29	4.08	6.1	-3.8	10.8	9.6	7.1
	25.5	7.90	3.14	2.70	1.55	11.15	4.91	4.17	8.5	-0.8	15.2	13.8	11.7
	23.8	7.60	3.14	2.78	1.54	11.90	5.22	4.16	6.2	-3.5	11.1	9.9	7.4
5	22.0	7.90	3.02	2.70	1.51	12.14	5.04	4.17	6.1	-3.4	11.2	10.1	7.30
	23.0	8.30	3.06	2.64	2.53	11.02	4.67	4.18	9.2	0.2	16.9	15.5	13.3
6	24.5	8.50	3.41	2.51	1.49	10.51	4.29	3.92	9.4	0.3	17.1	15.7	13.5
8	15.0	7.50	2.61	2.84	0.39	12.07	5.79	4.33	8.0	-2.0	14.8	13.4	11.1
10	35.3	7.14	2.61	1.94	0.57	12.59	6.05	4.87	6.4	-2.6	10.6	9.3	6.6
11	30.5	7.40	2.91	3.00	3.10	10.70	5.59	4.01	11.3	1.5	19.3	17.2	16.4
12	25.0	7.50	2.61	3.50	2.68	11.47	5.10	4.57	9.8	0.5	17.4	15.7	13.7
	25.0	7.50	2.61	3.54	2.72	11.46	5.09	4.65	9.8	0.5	17.2	15.5	13.6
13	25.5	7.10	3.13	3.06	2.49	11.76	5.77	4.51	6.4	-3.4	10.5	8.8	6.9
14	25.0	7.60	2.81	3.16	2.42	12.29	5.00	5.36	5.6	-2.9	9.5	8.1	5.1
15	26.5	7.01	2.51	3.75	3.93	12.57	6.08	5.06	6.6	-2.7	10.4	8.5	6.7
	26.0	7.25	2.46	3.71	3.86	11.69	5.86	4.89	9.6	0.4	16.0	13.9	12.6
	26.0	7.05	2.53	3.68	3.85	12.51	6.06	5.06	6.6	-2.7	10.6	8.6	6.8
16	25.0	7.10	2.81	3.35	2.45	11.61	5.67	4.87	8.1	-1.3	13.6	11.7	9.9
17	25.0	6.70	2.77	3.37	2.45	12.13	6.03	4.75	6.9	-3.1	11.3	9.5	7.6
19	25.5	7.30	2.78	3.35	2.42	11.36	5.47	4.88	9.0	-0.2	15.3	13.5	11.7
20	25.5	6.60	2.75	3.32	2.46	12.36	6.12	4.88	6.1	-3.8	9.9	8.1	6.1
21	24.5	7.10	2.68	3.49	2.51	11.40	5.64	5.05	9.2	-0.1	15.5	13.5	11.9
22	25.0	7.10	2.69	3.32	2.25	11.95	5.63	5.06	7.5	-1.8	12.6	10.9	8.7
23	24.5	7.00	2.82	3.48	2.98	11.49	5.77	5.04	8.3	-1.2	13.5	11.5	9.9
24	24.0	6.90	2.82	3.42	2.93	11.60	5.91	5.04	7.9	-1.7	12.8	10.8	9.3
25	24.0	7.55	2.84	3.42	3.03	10.84	5.25	5.34	9.7	1.2	16.4	14.3	12.7
	24.0	6.90	2.82	3.40	3.01	11.68	5.92	4.86	7.8	-1.9	12.8	10.8	9.3
26	26.0	7.10	2.79	3.49	2.77	11.39	5.63	5.04	8.7	-0.5	14.5	12.5	10.9
27	25.0	6.80	2.60	2.62	1.43	13.03	6.91	4.99	4.8	-4.8	7.2	5.6	3.4
28	25.0	8.30	2.96	3.38	2.75	11.02	4.61	5.04	8.9	0.8	15.6	13.9	11.7
29	25.5	8.00	2.93	3.71	3.10	11.27	4.74	4.73	8.7	0.0	15.1	13.4	11.4
30	23.0	7.10	3.18	3.58	3.17	11.00	5.91	5.02	7.9	-1.5	12.4	10.2	9.1
	23.0	6.90	3.11	3.59	3.19	11.26	6.08	5.03	7.4	-2.2	11.6	9.4	8.2
31	26.0	7.10	2.67	3.33	2.25	11.59	5.63	4.89	8.9	-0.5	15.1	13.2	11.4
32	26.0	7.00	2.68	3.34	2.28	12.56	5.73	4.89	5.9	-3.6	9.9	8.4	5.9
33	26.5	7.10	2.67	3.30	2.22	11.65	5.65	4.89	8.7	-0.7	14.8	12.9	11.1
34	25.0	7.30	3.04	3.50	3.40	10.72	5.56	5.03	9.4	0.3	15.5	13.2	12.1
35	23.0	7.30	3.10	3.60	3.46	10.93	5.71	5.32	8.2	-0.7	13.0	10.7	9.5
36	24.0	6.80	3.07	3.82	3.45	11.29	6.13	5.32	7.3	-2.1	11.1	8.7	7.6
37	24.5	7.50	3.26	3.90	3.42	11.10	5.68	5.01	7.2	-1.7	11.3	9.1	7.8
39	25.0	7.30	2.80	3.85	3.36	10.61	5.38	5.33	10.7	1.9	17.8	15.5	14.3
	23.0	7.30	2.79	3.76	3.55	11.61	5.36	5.03	8.0	-1.2	13.4	11.5	9.7
40	27.0	7.15	2.96	3.23	2.45	11.79	5.50	5.05	6.7	-2.5	10.9	9.2	7.0
41	24.0	7.20	3.17	3.52	3.11	11.29	5.83	5.02	7.1	-2.1	11.1	9.0	7.6
42	20.0	6.50	2.75	3.71	3.01	12.54	6.07	5.03	5.3	-4.8	8.5	6.7	4.7
43	23.0	6.90	2.74	3.97	2.92	11.47	5.68	5.33	8.4	-0.9	13.8	11.7	10.0
44	23.0	7.13	2.82	2.93	1.85	11.48	5.68	5.09	8.1	-1.1	13.8	12.0	10.0
45	23.5	7.01	2.73	3.52	2.70	11.28	5.54	5.34	9.0	-0.2	15.0	13.0	11.3
46	22.0	6.88	2.70	2.78	1.93	12.53	5.99	4.80	5.9	-4.0	9.9	8.4	6.0

TABLE 9.—Ion activities and saturation indices of apatites calculated by WATEQF using selected chemical analyses of water from wells in the Upper Floridan aquifer—Continued

Well number <sup>1</sup>	Water temperature, in °C	-Log <sub>10</sub> ion activity							Saturation index				
		H <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	CO <sub>3</sub> <sup>2-</sup>	F <sup>-</sup>	Fluor-apatite <sup>2</sup>	Hydroxy-apatite <sup>2</sup>	Carbonate fluorapatites <sup>3</sup>		
											Florida	North Carolina	Tennessee
47	22.0	7.22	2.66	2.77	1.85	11.81	5.72	4.94	8.1	-1.3	14.0	12.2	10.2
48	24.0	6.58	2.83	3.38	2.93	11.89	6.01	5.34	6.6	-2.9	10.5	8.5	6.7
49	22.0	6.55	2.79	3.81	3.06	11.92	6.09	5.33	6.7	-2.9	10.6	8.5	6.9
50	22.5	6.90	2.75	3.60	2.61	11.32	5.71	5.04	9.0	-0.6	15.2	13.1	11.6
51	23.0	7.60	2.88	2.99	2.24	11.23	5.49	5.07	8.6	-0.2	14.6	12.7	10.9
52	22.0	7.22	2.70	2.68	2.29	11.80	5.93	4.71	8.1	-1.5	13.9	12.1	10.3
53	20.5	7.20	2.63	2.90	3.45	11.43	5.67	4.48	9.8	-0.1	17.0	15.0	13.7
	20.5	7.10	2.72	2.98	3.52	11.64	6.74	4.59	8.6	-1.3	13.9	11.6	10.9
	20.8	7.18	3.05	3.42	3.65	11.04	5.67	4.85	8.5	-1.0	14.0	11.8	10.7
54	22.3	7.40	3.15	3.34	3.36	11.92	5.48	4.55	5.7	-3.9	9.4	7.7	5.7
55	24.0	8.86	4.59	4.84	1.90	10.22	3.52	3.75	4.5	-4.4	7.9	6.8	4.2
	26.5	8.90	4.87	4.96	1.93	9.86	3.46	3.89	4.1	-4.5	6.7	5.5	3.1
56	25.0	8.00	3.02	4.00	3.81	10.59	5.29	5.32	9.6	1.5	15.8	13.4	12.3
	20.5	7.60	3.07	3.95	3.85	10.96	5.69	5.02	8.5	-0.5	13.7	11.4	10.4
	21.0	8.10	3.03	3.99	3.82	10.65	5.21	5.02	9.7	1.2	16.1	13.9	12.7
57	20.9	7.90	3.23	3.55	3.90	11.29	5.16	4.84	6.9	-2.0	11.3	9.5	7.7
	21.5	7.80	3.24	3.55	3.94	10.35	5.23	4.84	9.7	0.8	16.0	13.8	12.8
	21.5	7.60	3.25	3.55	3.93	10.71	5.44	4.71	8.7	-0.6	14.2	12.0	11.0
58	19.9	8.00	3.30	3.63	3.86	10.27	5.14	5.31	9.1	0.8	14.9	12.5	11.4
	22.0	7.92	3.30	3.60	3.87	10.56	5.16	4.84	8.8	0.0	14.4	12.3	11.1
59	21.5	7.60	3.35	3.60	3.81	10.76	5.48	4.84	7.9	-1.3	12.7	10.5	9.4
	22.5	7.40	2.72	2.89	2.11	12.14	5.51	4.92	6.9	-2.3	11.8	10.3	7.9

<sup>1</sup> Well locations are shown in figure 29.

<sup>2</sup> Fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ),  $\log K_{\text{FAP}} = -66.79$  at 25 °C; hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ),  $\log K_{\text{HAP}} = -59.35$  at 25 °C; temperature dependence of the equilibrium constants was computed by WATEQF from the Van't Hoff equation, using  $\Delta H_{\text{FAP}} = 19.695$  and  $\Delta H_{\text{HAP}} = 17.225$  kilocalories per mole.

<sup>3</sup> Mineral formulas and equilibrium  $\log K_{\text{SP}}$  at 25 °C of carbonate apatites in citrate-extracted phosphate rocks (Chien and Black, 1976, tables 1 and 4):

Florida— $\text{Ca}_{9.71}\text{Na}_{0.21}\text{Mg}_{0.08}(\text{PO}_4)_{5.19}(\text{CO}_3)_{0.81}\text{F}_{2.32}$ ,  $\log K_{\text{SP}} = -117.8$

North Carolina— $\text{Ca}_{9.54}\text{Na}_{0.33}\text{Mg}_{0.13}(\text{PO}_4)_{4.80}(\text{CO}_3)_{1.20}\text{F}_{2.48}$ ,  $\log K_{\text{SP}} = -114.4$

Tennessee— $\text{Ca}_{9.86}\text{Na}_{0.11}\text{Mg}_{0.04}(\text{PO}_4)_{5.56}(\text{CO}_3)_{0.44}\text{F}_{2.18}$ ,  $\log K_{\text{SP}} = -118.7$ .

No correction of  $\log K_{\text{SP}}$  was made for solution temperatures different from 25 °C, due to lack of enthalpy data for the minerals.

known, so the choice of solubility product constant to use in computing the S.I. is questionable. Furthermore, the possibility that an amorphous calcium phosphate compound is controlling  $\text{F}^-$  concentrations cannot be dismissed, even though a study by Gulbrandsen and others (1984) casts doubt on the long-term stability of these compounds, even in a freshwater environment. Therefore, the apparent oversaturation of ground water in the Upper Floridan aquifer with respect to fluoride-bearing apatites may not be real; some species of carbonate fluorapatite may be in equilibrium with the ground water. More data on both dissolved-phosphate concentrations in ground water and composition of apatite species in the aquifer are required to determine whether or not mineral equilibria actually control  $\text{F}^-$  concentrations in the Upper Floridan aquifer.

#### SILICA AND ALUMINUM

Concentrations of dissolved silica in water from the Upper Floridan aquifer vary from about 1 to about 80

mg/L (about 0.02 to about 1.33 mmol as  $\text{SiO}_2$ ), values fairly typical of natural waters (Hem, 1970, p. 109). The general distribution of dissolved silica in the Upper Floridan is shown in figure 30. The data along flow paths shown in figure 30 are used in a later discussion of the chemical controls on dissolved aluminum in the Upper Floridan. The highest concentrations of dissolved silica generally occur in the Upper Floridan aquifer in Georgia and South Carolina, where chalcedony and aluminosilicate minerals may be locally more abundant. In these areas, recharge from underlying sand aquifers may increase dissolved-silica concentrations in the Upper Floridan, as silica concentrations in the sand aquifers locally range from about 20 to 50 mg/L (Lee, 1984, table 3). At 25 °C, concentrations of dissolved silica near 0.10 mmolar (6 mg/L) are in equilibrium with quartz, and concentrations of 0.50 mmolar (30 mg/L) are near equilibrium with chalcedony (fig. 31). In 905 analyses of water from the Upper Floridan aquifer, 95 percent of the measured silica concentrations were in the range 5.5 to

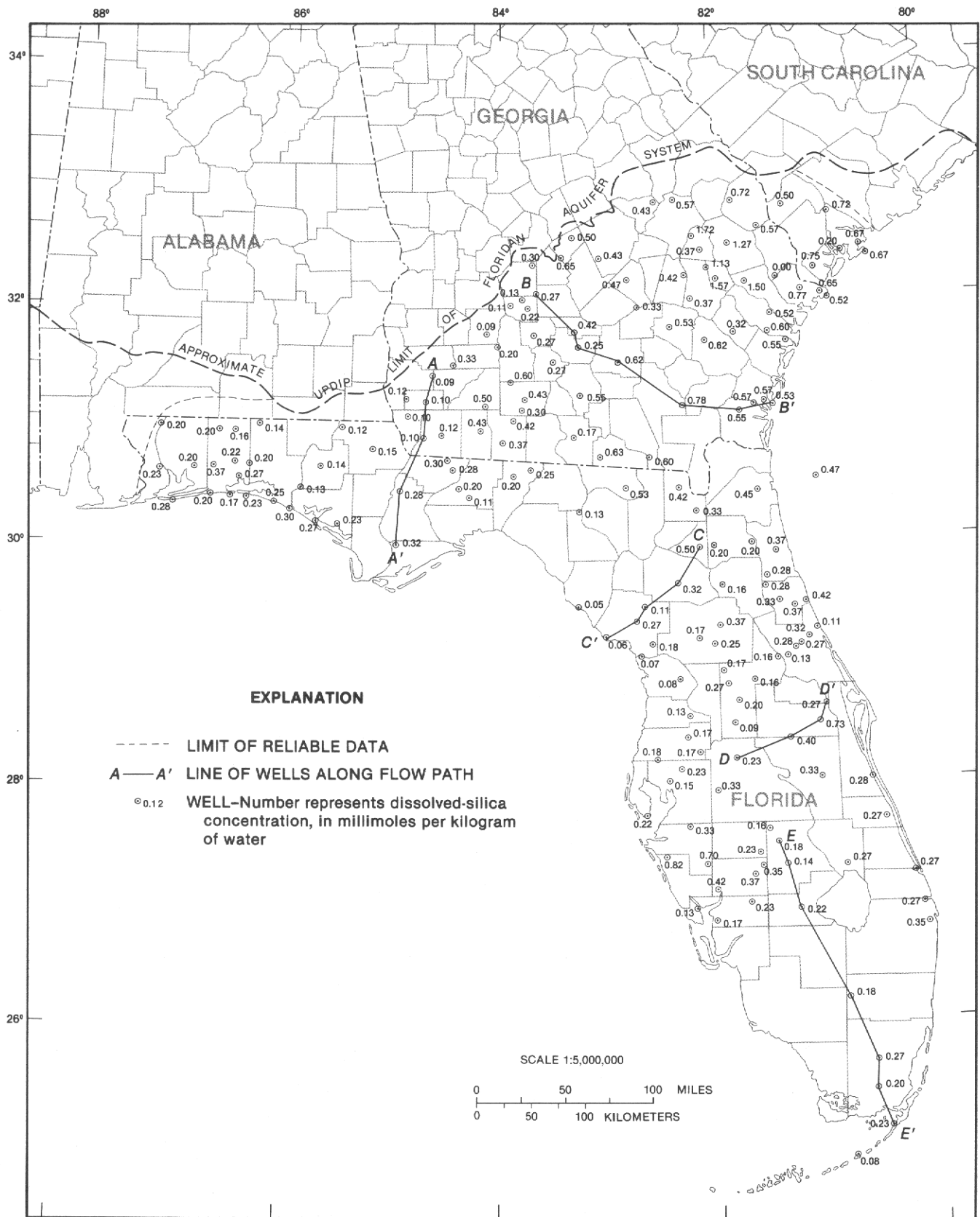


FIGURE 30.—Concentrations of dissolved silica in water samples from selected wells in the Upper Floridan aquifer.



37 mg/L; the median concentration was 14 mg/L. The data plotted in figure 31 suggest that the lower limit of dissolved silica is quartz solubility and the upper limit of dissolved silica is the solubility of chalcedony. Concentrations of dissolved silica higher than 40 mg/L may be the result of local contamination, dissolution of local sources of highly soluble silicate phases(?), or water-sampling and analytical errors.

As mentioned in a previous section, the high  $\text{Na}^+$  concentrations in the Upper Floridan aquifer in the Florida Panhandle do not appear to result from weathering of silicate minerals. As shown in figure 30, dissolved-silica concentrations in this area are near the median value for the entire aquifer; also, dissolved-silica concentrations do not increase in a downgradient direction. A water sample from a well in the Upper Floridan aquifer in eastern Escambia County, Fla., was analyzed for dissolved aluminum (fig. 32) and therefore could be used to calculate saturation indices of sodium-silicate minerals using WATEQF and the log  $K_{\text{eq}}$  data of table 10. The calculated results for the shallow monitor well (sampled on March 15, 1971) are shown below:

Mineral name	Formula	Saturation index
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	+0.99
Na-beidellite	$\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	+3.38
(Low) albite	$\text{NaAlSi}_3\text{O}_8$	+1.45
(Aberdeen) Montmorillonite	$(\text{H}, \text{Na}, \text{K})_{0.42}\text{Mg}_{0.45}\text{Fe}^{3+}_{0.34}\text{Al}_{1.47}\text{Si}_{3.82}\text{O}_{10}(\text{OH})_2$	+5.06
(Belle Fourche) Montmorillonite	$(\text{H}, \text{Na}, \text{K})_{0.28}\text{Mg}_{0.29}\text{Fe}^{3+}_{0.23}\text{Al}_{1.58}\text{Si}_{3.93}\text{O}_{10}(\text{OH})_2$	+5.47

These results suggest that the excess  $\text{Na}^+$  is not due to dissolution of these phases, if they occur in the rocks of the area. If some unidentified sodium-silicate phase were dissolving, the silica added by dissolution must be precipitating almost simultaneously in some more stable phase(s), since dissolved-silica concentrations are not increasing. Assuming that the major control on silica concentrations in the Upper Floridan aquifer is the solubility of quartz or chalcedony, then the dissolution of sodium silicates should lead to formation of chalcedony cements or quartz grain overgrowths. Lithologic logs of test wells in Escambia and Santa Rosa Counties (Hull and Martin, 1982) do not mention the occurrence of chalcedony cements or overgrowths in the rocks of the Upper Floridan aquifer, although detailed microscopic studies were not made. Without detailed mineralogic and petrographic studies of the aquifer materials in the panhandle area, the presumption that silicate weathering does not cause the high  $\text{Na}^+$  concentrations in the area cannot be proven correct; however, the available data and calculations cited above tend to support the presumption.

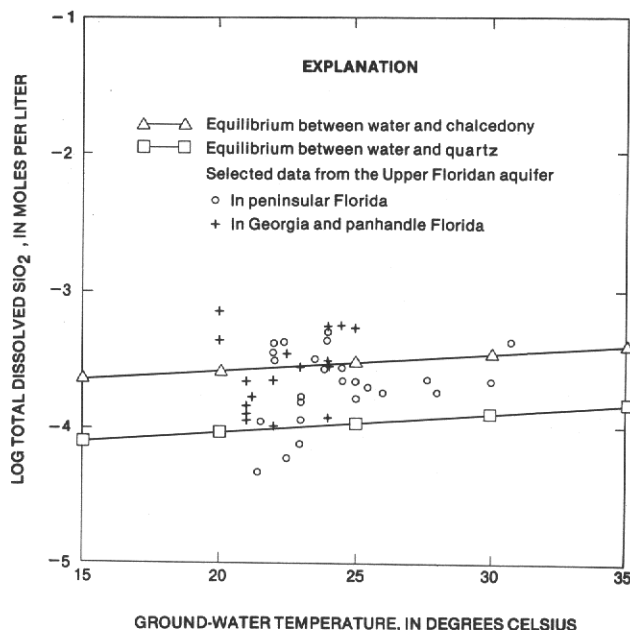


FIGURE 31.—Relation between dissolved silica and temperature in water samples from selected wells in the Upper Floridan aquifer.

The available data on dissolved-aluminum concentrations in the Upper Floridan aquifer are scarce and are not well distributed over the study area (fig. 32). Only 144 analyses of dissolved aluminum were made of water samples from 107 wells during the period 1970–82. The maximum reported concentration was 0.3 mg/L, but 95 percent of the measured concentrations were less than 0.1 mg/L (about 3.7 mmol per kilogram of water). The 44 analyses of dissolved aluminum shown in figure 32 were selected to give maximum areal coverage; where two (or more) proximate wells had analyses, the analysis from the deeper well was selected. Because “dissolved” aluminum concentrations were analyzed from water samples that had been treated at the well site by passing them through a 0.45- $\mu\text{m}$  filter and acidifying to pH 2.0 with concentrated nitric acid, some uncertainties are introduced in interpretation of the aluminum data. Some particulate aluminum phases may pass through a 0.45- $\mu\text{m}$  filter (Kennedy and others, 1974; Barnes, 1975). Dissolved-aluminum concentrations of about 0.1 to 1 mmol in water with pH between 7 and 8 are in equilibrium with crystalline  $\text{Al}(\text{OH})_3$  (gibbsite) (fig. 33; Reesman and others, 1969; Hemingway, 1982). The data plotted in figure 33 indicate that some water samples from the Upper Floridan aquifer contained almost an order of magnitude too much “dissolved” aluminum to be in equilibrium with gibbsite.

To test the possibility that other aluminum or aluminosilicate phases might be controlling dissolved-aluminum concentrations, the 44 selected analyses were processed





TABLE 10.—Summary of thermochemical data and saturation indices for selected mineral phases, calculated by WATEQF from 44 analyses of ground water from wells in the Upper Floridan aquifer  
[kcal/mol, kilocalories per mole]

Phase	Log $K_{eq}$ (equilibrium constant) at 25 °C	$\Delta H^\circ_r$ (enthalpy), in kcal/mol	Saturation index			Standard deviation
			Mean	Maximum	Minimum	
Quartz	-3.973	5.35	0.464	0.943	-0.137	0.264
Chalcedony	-3.523	4.615	0.011	0.485	-0.400	0.262
Silica glass	-2.969	3.56	-0.548	-0.080	-1.149	0.260
Gibbsite	-33.91	17.25	1.193	2.357	-0.035	0.434
Al(OH) <sub>3</sub> , amorphous	-31.61	12.99	-1.127	0.036	-2.284	0.426
Kaolinite	-40.29	52.81	5.789	7.684	3.011	0.980
Halloysite	-37.02	48.36	2.498	4.364	-0.205	0.967
(Low) Albite	-20.40	26.67	0.590	2.886	-1.550	1.059
Microcline	-22.16	31.63	1.262	3.081	-0.932	0.934
Na-beidellite	-49.33	62.34	6.486	9.036	3.333	1.275
Ca-montmorillonite	-49.08	60.46	6.169	8.724	2.920	1.287
Belle Fouche montmorillonite	-34.97	0.0	6.604	8.715	4.309	1.096
Aberdeen montmorillonite	-29.78	0.0	5.973	8.118	3.623	1.116
Wairakite	-26.62	26.14	-2.782	-0.355	-4.895	1.218
Laumontite	-30.96	39.61	1.618	4.126	-0.644	1.246
Analcime	-16.27	21.21	-0.032	0.994	-1.867	0.952
Muscovite	-56.03	72.81	7.644	10.643	4.669	1.310
Phillipsite	-19.86	0.0	-0.626	1.346	-2.915	1.025
Pyrophyllite	-46.68	59.72	5.145	7.754	2.102	1.301
Leonhardite	-75.47	90.83	16.839	21.924	12.123	2.520

by WATEQF using free energies and enthalpies given in table 11. The program calculated S.I. for mineral phases that might be present in trace quantities in the Upper Floridan aquifer (table 10). A temperature of 25 °C was

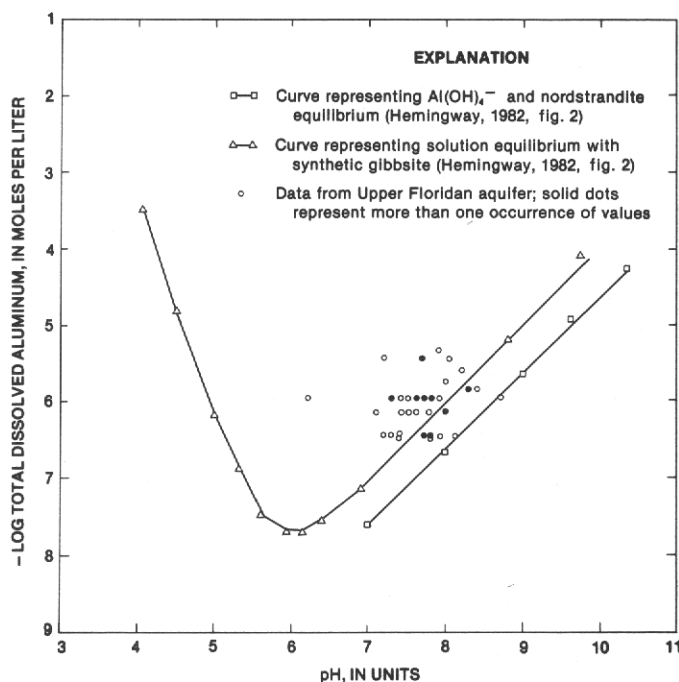


FIGURE 33.—Relation between dissolved aluminum and pH in water samples from selected wells in the Upper Floridan aquifer.

chosen for the log  $K_{eq}$  values since most of the ground water in the Upper Floridan aquifer is near this temperature (fig. 2). The summary statistics in table 10 indicate that amorphous Al(OH)<sub>3</sub> is the only aluminum-containing phase that is consistently undersaturated in the water samples analyzed. Adularia (a K<sup>+</sup>-feldspar variety), albite, halloysite, and phillipsite (a Na<sup>+</sup>, K<sup>+</sup>-bearing zeolite) are often undersaturated, indicating that these phases could increase dissolved-aluminum concentrations if the minerals actually are present in the aquifer. The mean saturation index for gibbsite is near zero, which may indicate that gibbsite controls aluminum concentrations in some places. Drever (1982, fig. 5-4), however, shows that gibbsite is an equilibrium control on dissolved aluminum only when activities of dissolved silica (H<sub>4</sub>SiO<sub>4</sub>) are less than approximately 10<sup>-4.5</sup> (less than 2 mg/L in dilute solutions). At higher dissolved-silica concentrations, the total activity of dissolved-aluminum species should be much less, owing to the formation of stable aluminosilicate phases. The data in table 10 show that only halloysite and albite are not highly oversaturated in some of the water samples analyzed. The amount of oversaturation may be due to the passage of particulate Al-bearing phases through the 0.45- $\mu$ m filter, thus increasing the concentration of "dissolved" aluminum reported.

An alternative approach to evaluating dissolved SiO<sub>2</sub> and Al<sup>3+</sup> in the Floridan aquifer system is the method of

TABLE 11.—Standard-state (25 °C, 1 atmosphere) Gibbs free energies ( $\Delta G^\circ$ ) and enthalpies ( $\Delta H^\circ$ ) of selected phases in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ [kcal/mol, kilocalories per mole; J mol<sup>-1</sup>, joules per mole. Dashes indicate calculation not performed]

Phase or species	Mineral name	$\Delta G^\circ$ , in kcal/mol	$\Delta H^\circ$ , in kcal/mol	Source <sup>1</sup>
H <sub>2</sub> O		-56.69	-68.32	R
OH <sup>-</sup>		-37.60	-54.98	R
Na <sup>+</sup>		-62.60	-57.43	R
K <sup>+</sup>		-67.52	-60.27	R
Ca <sup>2+</sup>		-132.30	-129.74	R
Al <sup>3+</sup>		-116.97	-126.91	R
Al(OH) <sup>2+</sup>		-166.8	-183.3	B <sup>2</sup>
Al(OH) <sub>2</sub> <sup>+</sup>		-216.57	----	B <sup>2</sup>
Al(OH) <sub>4</sub> <sup>-</sup>		-312.35	-356.13	B <sup>2</sup>
H <sub>4</sub> SiO <sub>4</sub> (aqueous)		-312.62	-348.95	R
SiO <sub>2</sub>	quartz	-204.66	-217.66	R
SiO <sub>2</sub>	glass	-203.29	-215.87	R
SiO <sub>2</sub>	chalcedony	-204.0	-216.9	P <sup>2</sup>
Al(OH) <sub>3</sub>	gibbsite	-276.03	-309.07	R
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	kaolinite	-908.07	-984.73	R
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	halloysite	-903.61	-980.28	R
Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	pyrophyllite	-1,258.58	-1,347.94	R
NaAlSi <sub>3</sub> O <sub>8</sub>	(low) albite	-887.12	-940.52	R
NaAlSi <sub>2</sub> O <sub>6</sub> •H <sub>2</sub> O	analcime	-738.94	-791.07	R
Na <sub>0.33</sub> Al <sub>2.33</sub> Si <sub>3.67</sub> O <sub>10</sub> (OH) <sub>2</sub>	Na-beidellite	-1,282.98	-1,372.1	G&M <sup>3</sup>
KAlSi <sub>3</sub> O <sub>8</sub>	microcline	-894.44	-948.30	R
KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	muscovite	-1,338.59	-1,428.48	R
CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> •2H <sub>2</sub> O	wairakite	-1,476.9	-1,580.74	P <sup>2</sup>
CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> •4H <sub>2</sub> O	laumontite	-1,596.2	-1,730.85	P <sup>2</sup>
Ca <sub>2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> •7H <sub>2</sub> O	leonhardite	-3,154.19	-3,404.99	R
Ca <sub>0.17</sub> Al <sub>2.33</sub> Si <sub>3.67</sub> O <sub>10</sub> (OH) <sub>2</sub>	Ca-montmorillonite	-1,283.82	-1,372.7	G <sup>3</sup>

<sup>1</sup> R, Robie and others (1978), except  $\Delta G^\circ$  water = -237,181 J mol<sup>-1</sup>.<sup>2</sup>  $\Delta G^\circ$ ,  $\Delta H^\circ$  computed from data in this table and log K data in: B, Ball and others (1978); P, Plummer and others (1978).<sup>3</sup>  $\Delta G^\circ$  computed from data in this table and "apparent" equilibrium log K for kaolinite-Ca-montmorillonite (log K = -12.5 (Garrels, 1967)) and kaolinite-Na-beidellite (log K = -7.0 (Garrels and MacKenzie, 1967)).  $\Delta H^\circ$  values calculated from  $\Delta G^\circ$  and estimates of entropy given in footnotes e and f in table 12 of Helgeson (1969).

Thompson (1955, in Drever, 1982, p. 97), who suggested that Al<sub>2</sub>O<sub>3</sub> might be treated as a conservative component in the weathering of silicates. That is, silicate minerals are assumed to dissolve incongruently to new minerals while aluminum is retained among the solid phases. Using this assumption, stability diagrams of the systems K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O at 25 °C were prepared (figs. 34A-34C) using the data listed in table 11. The data in table 11 are consistent with diagrams drawn by Drever (1982, figs. 5-5, 5-8) and the solubilities of quartz and amorphous silica used by WATEQF. Chemical data from wells along lines following several flow paths (fig. 30) were selected, the log activities of K<sup>+</sup>, H<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and H<sub>4</sub>SiO<sub>4</sub> were calculated by WATEQF, and selected ratios were plotted against the activity of H<sub>4</sub>SiO<sub>4</sub> (fig. 34). While the wells along flow paths A-A', B-B', and C-C' are generally representative of freshwater parts of the aquifer, wells in downgradient segments of flow

paths D-D' and E-E' are representative of saline parts of the aquifer system. Data from wells along flow path C-C' show the least change in Na<sup>+</sup>/H<sup>+</sup> or K<sup>+</sup>/H<sup>+</sup> activities, as this flow path is through an unconfined, highly permeable part of the aquifer system. The data from the freshwater areas tend to cluster around the logarithmic (log) value of the activity ratio of K<sup>+</sup>/H<sup>+</sup> of about 3 and the log value of the activity ratio of Na<sup>+</sup>/H<sup>+</sup> of about 4; the ratios from the more saline areas are about 1 log unit higher.

Figure 34 indicates no simple pattern of incongruent silicate weathering. The data from the freshwater flow paths A-A', B-B', and C-C' do not exhibit systematic changes; most of the data plot within the kaolinite stability field. The data plotted in figure 34C show no systematic changes in the Ca<sup>2+</sup>/(H<sup>+</sup>)<sup>2</sup> activity ratio. The lack of trend in the data plotted in figure 34C does not rule out the possibility of diagenesis of calcium-bearing silicates in the aquifer system. Silicate weathering is

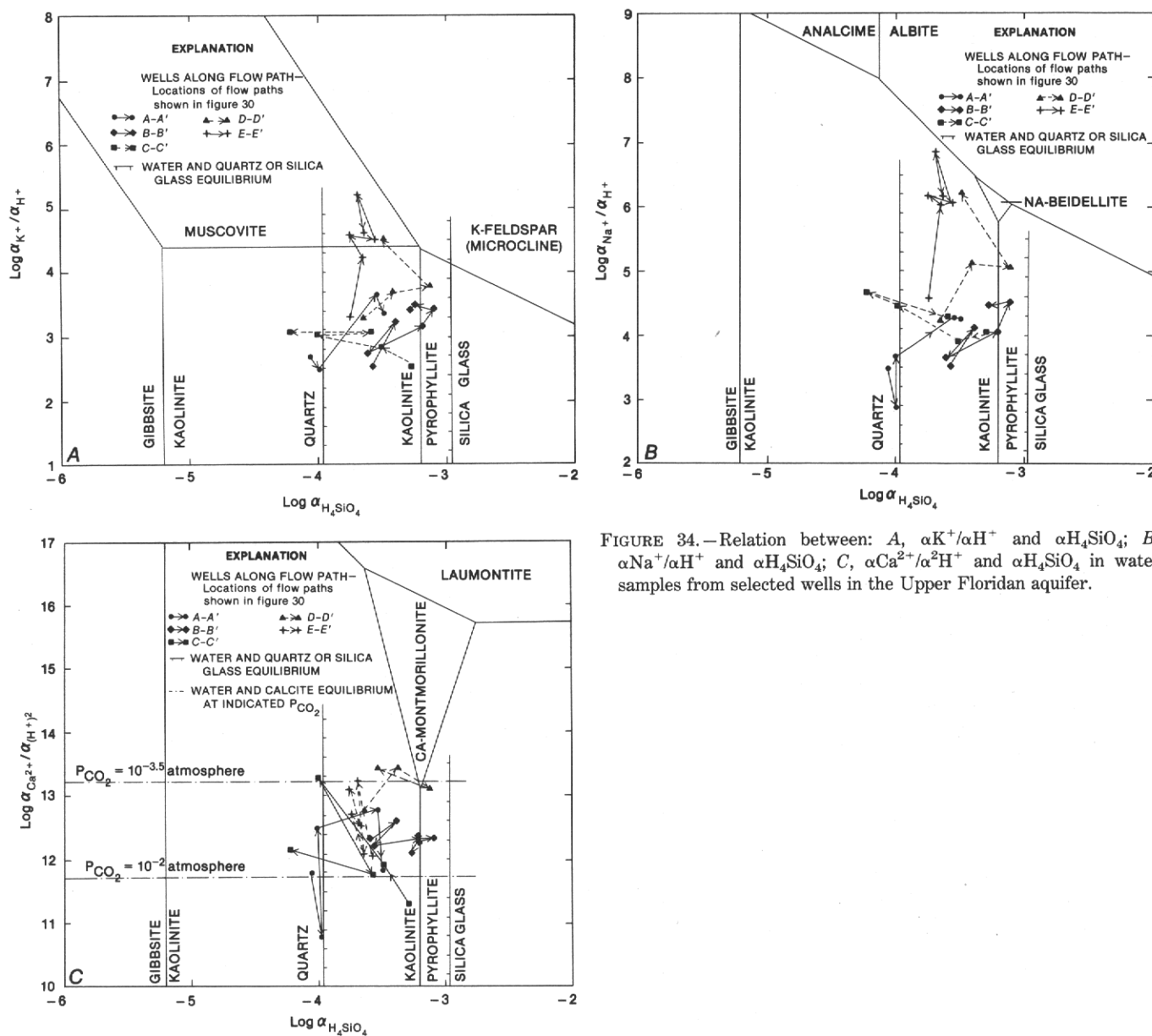


FIGURE 34.—Relation between: A,  $\alpha_{K^+}/\alpha_{H^+}$  and  $\alpha_{H_4SiO_4}$ ; B,  $\alpha_{Na^+}/\alpha_{H^+}$  and  $\alpha_{H_4SiO_4}$ ; C,  $\alpha_{Ca^{2+}}/\alpha_{H^+}^2$  and  $\alpha_{H_4SiO_4}$  in water samples from selected wells in the Upper Floridan aquifer.

probably occurring, but concentrations of calcium and hydrogen ions are greatly influenced by changes in carbonate equilibria. Small changes in concentrations of these ions due to silicate dissolution are masked by the much larger effects of dedolomitization in most of the aquifer system. In contrast, the data from the more saline flow paths *D-D'* and *E-E'* show systematic changes—the upgradient data plot near the middle of the kaolinite field, and the downgradient data plot near phase boundaries in both figures 34A and 34B. In figure 34B the downgradient data from flow paths *D-D'* and *E-E'* plot approximately parallel to the kaolinite-Na-beidellite phase boundary, indicating that the boundary for smectites in the aquifer system may occur at slightly lower dissolved silica activities. The downgradient pro-

gression toward the smectite stability field (fig. 34B) is typical of the general pattern of feldspar weathering (Drever, 1982, p. 141–157 and 163–198, cites examples from the literature). However, the apparent progression toward the kaolinite-muscovite phase boundary (fig. 34A) is not necessarily real and may be related to the choice of minerals used to construct the two-dimensional stability diagram.

Given the uncertainties in composition, equilibrium solubility, and distribution of silicate minerals within the aquifer system, only the most general conclusions can be drawn from the available silica and aluminum data. Dissolved-silica concentrations appear to be controlled primarily by the solubility of chalcedony, although quartz may be the control in parts of the Floridan where

TABLE 12.—Summary statistics for nitrogen (N) and phosphorus (P) concentrations in water from the Upper Floridan aquifer, calculated from selected water analyses and reported as elemental N or P

Species		Number of samples	Concentration, in milligrams per liter					
			Maximum	75 percentile	Median	Mean	25 percentile	Minimum
Total - N	(F) <sup>1</sup>	26	4.7	0.80	0.52	1.07	0.31	0.08
Ammonia (NH <sub>4</sub> )-N	(F)	44	2.1	0.52	0.29	0.40	0.15	0.01
Organic (Org)-N	(F)	35	4.6	0.37	0.20	0.45	0.05	0
Nitrite (NO <sub>2</sub> )-N	(F)	112	0.06	<0.01	0	<0.01	0	0
Nitrate (NO <sub>3</sub> )-N	(F)	328	3.16	0.09	0	0.14	0	0
NH <sub>4</sub> + Org (KJD)-N	(F)	36	4.7	1.03	0.55	0.83	0.33	0.08
NO <sub>2</sub> +NO <sub>3</sub> -N	(F)	56	3.0	0.05	0.05	0.19	0.01	0
Total - N	(UF)	273	8.67	1.61	1.45	1.48	1.18	0.06
NH <sub>4</sub> -N	(UF)	293	2.1	1.25	1.0	0.86	0.41	0
Org-N	(UF)	275	1.2	0.35	0.2	0.24	0.07	0
NO <sub>2</sub> -N	(UF)	331	0.55	<0.01	<0.01	0.01	<0.01	0
NO <sub>3</sub> -N	(UF)	332	7.6	0.02	0	0.31	0	0
KJD-N	(UF)	270	2.54	1.5	1.34	1.11	0.84	0
NO <sub>2</sub> +NO <sub>3</sub> -N	(UF)	260	7.78	0.08	0.01	0.37	<0.01	0
Total - P	(F)	34	2	0.07	0.02	0.10	<0.01	0
Orthophosphate (PO <sub>4</sub> )-P	(F)	83	2	0.05	0.02	0.05	<0.01	0
Total - P	(UF)	270	1.8	0.08	0.06	0.07	0.03	0
PO <sub>4</sub> -P	(UF)	261	1.2	0.08	0.05	0.06	0.02	0

<sup>1</sup> F, filtered water sample; UF, unfiltered (whole) water sample.

ground-water flow is very sluggish. Aluminum concentrations are likely very low, possibly controlled by (1) the solubility of gibbsite or (2) the alteration of kaolinite to mixed-layer clays (smectites).

#### NUTRIENTS

The occurrence of the principal nutrients, nitrogen (N) and phosphorus (P) species, in the Upper Floridan aquifer was investigated by retrieval of all N and P data available for the 601 wells used to describe the major ion chemistry. A total of 648 analyses (from 591 wells) of various N and P species were compiled into a data set and statistically analyzed using procedures available in SAS (SAS Institute, 1979). Table 12 reports summary statistics for both total and dissolved nutrient-species concentrations. The 648 analyses contained some qualified values. Especially common were concentrations reported as less than a threshold value (detection limit). For "less than" qualified values, a concentration of one-half the threshold value was substituted before any statistical tests were performed. The data in table 12 show that except for dissolved nitrate, the preponderance of analyses of N and P species were made on whole water samples; thus, bacteria in the water were analyzed, along with any trace solids (minerals) containing N or P forms. These whole-water analyses are probably representative of "available" N, however, since microorganisms can easily reduce and assimilate organic N. The orthophosphate (PO<sub>4</sub>) in organic material (or minerals) is readily assimilated in any case.

The data shown in table 12 indicate that low concentrations of P occur throughout the Upper Floridan aquifer; 75 percent of the samples contained less than 0.1 mg/L of P. At these low concentrations, P dissolved in ground water may be limiting to the growth of bacterial populations in the aquifer, if mineral sources of P are not available. Bacteria contain mole ratios of carbon(C):N:P of 47.3:7.3:1 (Fenchel and Blackburn, 1979, table III, p. 16). This means that to assimilate, for example, 0.05 mg/L of P completely, the bacterial population needs only 0.17 mg/L of N and 0.92 mg/L of C. In the Upper Floridan aquifer, the median concentration of NH<sub>4</sub> nitrogen in more than 290 samples was 1.0 mg/L (table 12) and the median concentration of dissolved organic carbon in 48 samples was 4.0 mg/L (table 18). Both are well above the amounts required for a bacterial population to assimilate 0.05 mg/L of P, the median concentration of P, even if other sources of N and C were not available. Bacterial assimilation of the median concentration of P calculated for filtered water samples (0.02 mg/L, table 12), that is, P in "true" solution, would require even less N or C in solution.

The sources of the various N and P species in the Upper Floridan aquifer are not well defined over the aquifer's areal extent. As described previously, the Upper Floridan aquifer contains trace amounts of phosphate minerals in many areas; the overlying Hawthorn Formation contains economic concentrations of phosphate minerals in southwestern and north-central Florida. Wherever recharge through the Hawthorn can